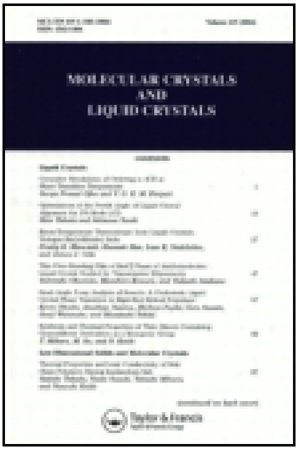

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Order Parameters of Schiff Base Azo Dyes in Nematic Liquid Crystalline Hosts

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Order Parameters of Schiff Base Azo Dyes in Nematic Liquid Crystalline Hosts

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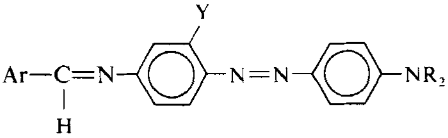
The order parameters (S) of a number of Schiff base azo compounds having the structure



where Ar = 4-cyanophenyl, 4-nitrophenyl, 5-chlorothienyl, or 2-pyridyl; Y = hydrogen, methyl, or methoxy; R = methyl, ethyl, *n*-butyl, or *n*-hexyl; NR_2 = N-pyrrolidinyl have been determined in two different nematic liquid crystalline hosts both of which have a positive dielectric anisotropy. The results are discussed in terms of the effects of the dye structure on the order parameter.

INTRODUCTION

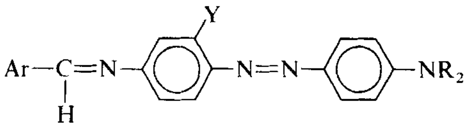
Since the first report on guest-host interaction between a pleochroic dye and a liquid crystalline host by Heilmeier and Zanoni,[1] there has been a continuing interest in this phenomenon.[2–8]

The order parameter (S) is a measure of how well a dye molecule is aligned with the orientation direction of the nematic liquid crystalline host. If the dye molecules are chosen such that their geometric long axis corresponds to the direction of absorption polarization and the contributions to the absorption caused by molecular polarization in the perpendicular direction are small, then the order parameter can be obtained using plane polarized light by means of the formula[2, 10]

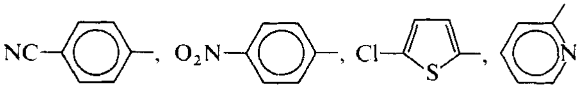
$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \qquad (1)$$

where $A_{\parallel}$ is the optical density of the dye at its absorption maximum (λ_{max}) when the polarization is parallel to the alignment direction and $A_{\perp}$ is the optical density at λ_{max} when the polarization is perpendicular to the alignment direction.

There is a correlation between the length of the dye molecule and its order parameter.[2, 7] Dye structure[7] and the liquid crystalline host[8] are also important factors which influence dye alignment. To gain a better understanding of the role of dye structure on guest-host interactions, we have synthesized a number of Schiff base azo dyes of the following structure,



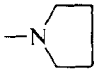
Ar =



$Y = H, CH_3, OCH_3$

$R = CH_3, C_2H_5, n\text{-}C_4H_9, n\text{-}C_6H_{13}$

$NR_2 =$



and studied the guest-host interactions between them and selected nematic liquid crystalline hosts.

EXPERIMENTAL

A Measurements

The cell used consisted of two glass plates, 2.5 × 2.5 cm in size, each having a transparent conductive layer of indium-doped tin oxide onto which a SiO_x layer was evaporated at an angle of 30° to the horizontal to give parallel alignment.[11, 12] The top plate had two diagonally placed holes (1 mm

TABLE I

Physical properties of liquid crystalline hosts

Host	Composition	Nematic range °C	Dielectric constants[15] $\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
S	A mixture containing 85 wt % of a 70:30 molar mixture of 4-methoxybenzylidene-4′-butylaniline (MBBA) and 4-ethoxybenzylidene-4′-butylaniline (EBBA) and 15 wt % of 4-ethoxybenzylidene-4′-aminobenzonitrile.[11]	−9 to 40	8.8	5.7
E	Hoffman-LaRoche RO-TN-101, an ester mixture.	0 to 71	24.9[a]	7.2[a]

[a] Hoffman-LaRoche product bulletin.

diameter) for filling. The plates were separated by 12 μm spacers and epoxy-sealed together. The cells were flushed with acetone, methanol, and nitrogen prior to filling. The dye concentration was ca. 0.3 wt %.

The optical density was measured at 22 ± 1°C on a Cary 14 spectrophotometer equipped with a Glan-Foucault calcite polarizer using a modified sample holder which has been previously described.[13] Corrections were made for host and cell absorption, reflection, and scattering.

B Materials

The syntheses and characterization of these dyes will be described elsewhere.[16] All compounds were made analytically pure by column chromatography, using 60–200 mesh silica gel (MCB), and by repeated recrystallization until silica gel thin layer chromatography (Eastman) showed only one spot in several solvents and had satisfactory elemental analyses.

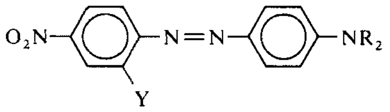
The nematic liquid crystalline hosts used in this study as well as some of their relevant physical properties are listed in Table I. Host S is a Schiff base mixture and Host E is a commercial ester mixture. Both hosts have a positive dielectric anisotropy.

RESULTS AND DISCUSSIONS

For comparison purposes, the order parameters of some of the Schiff base azo dye precursors have also been determined in the same selected nematic liquid crystalline hosts. The order parameters of some substituted 4-nitro-4′-dialkylaminoazobenzenes in Host *S* and Host *E* and those for 4-amino-4′-dialkylaminoazobenzenes in Host *E* are summarized in Tables II and III,

TABLE II

Order parameters and absorption maxima of 4-nitro-4′-dialkylaminoazobenzenes in hosts *E* and *S*



Dye	*Y*	*R*	*S*(Host *E*)	λ^{a}_{nm}(Host *E*)	*S*(Host *S*)	λ^{b}_{nm}(Host *S*)
XXV	CH_3	n-C_4H_9	0.42	508	0.40	506
XXVI	OCH_3	n-C_4H_9	0.39	515	0.34	516
XXVII	H	n-C_6H_{13}	0.46	507	0.48	507
XXVIII	CH_3	n-C_6H_{13}	0.41	508	0.42	509
XXIV	OCH_3	n-C_6H_{13}	0.38	515	0.31	519

[a] Absorption maximum in the nematic host.

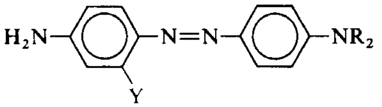
[b] Data from Ref. 7.

respectively, while those for the Schiff-base azo compounds derived from these precursors are listed in Table IV. In Host *E*, the amino-azo-benzenes generally have lower order parameters than the corresponding nitro-azobenzene compounds. Also, in Host *E*, the Schiff base azo compounds have order parameters very much higher than those of their amine precursors.

The order parameters of the Schiff base azo dyes in Table IV vary with the dye structure in a systematic manner; a phenomenon consistent with the effect of dye structure on order parameter in a nematic liquid crystalline

TABLE III

Order parameters and absorption maxima of 4-Amino-4′-dialkylaminoazobenzenes in host *E*.

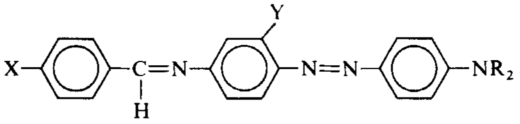


Dye	*Y*	*R*	*S*	λ(nm)[a]
XXX	CH_3	C_2H_5	0.41	427
XXXI	OCH_3	C_2H_5	0.32	427
XXXII	CH_3	n-C_4H_9	0.32	425
XXXIII	OCH_3	n-C_4H_9	0.26	427
XXXIV	H	n-C_6H_{13}	0.40	420
XXXV	OCH_3	n-C_6H_{13}	0.22	428

[a] Wavelength at which order parameter was obtained.

TABLE IV

Order parameters and absorption maxima of Schiff base azo dyes in Host *E*.



Dye	*X*	*Y*	*R*	*S*	λ(nm)[a]
I	NO_2	H	C_2H_5	0.66	475
II	NO_2	CH_3	C_2H_5	0.61	482
III	NO_2	OCH_3	C_2H_5	0.65	500
IV	NO_2	H	n-C_4H_9	0.62	475
V	NO_2	CH_3	n-C_4H_9	0.59	485
VI	NO_2	OCH_3	n-C_4H_9	0.57	487
VII	NO_2	H	n-C_6H_{13}	0.60	481
VIII	NO_2	CH_3	n-C_6H_{13}	0.59	485
IX	NO_2	OCH_3	n-C_6H_{13}	0.54	492
X	CN	H	CH_3	0.67	455
XI	CN	H	C_2H_5	0.64	468
XII	CN	CH_3	C_2H_5	0.62	475
XIII	CN	OCH_3	C_2H_5	0.59	479
XIV	CN	H	$(CH_2)_2$ N-pyrrolidinyl	0.64	465
XV	CN	H	n-C_4H_9	0.61	470
XVI	CN	CH_3	n-C_4H_9	0.58	472
XVII	CN	OCH_3	n-C_4H_9	0.58	482
XVIII	CN	H	n-C_6H_{13}	0.60	473
XIX	CN	CH_3	n-C_6H_{13}	0.58	473
XX	CN	OCH_3	n-C_6H_{13}	0.58	482

host as described previously[7] Thus, for a given series of Schiff base azo compounds, the order parameters decrease with increasing length of the N,N-dialkyl group, e.g. *S*(X) > *S*(XI) > *S*(XV) > *S*(XVIII), and *S*(I) > *S*(IV) > *S*(VII). These results are consistent with the structural properties of the N,N-dialkyl end group. As the N-alkyl chain lengthens, the N,N-dialkylamine group tends to occupy a greater effective volume than the simple N,N-dimethylamino group, which prevents the long molecular axis of the guest from aligning as well with the host director. This poorer alignment results in a lower order parameter. When the ethyl chain ends are linked together to form a pyrrolidine ring which minimizes off-axis interactions of the guest with the host, the order parameter *S*(XIV) is comparable to that of N,N-diethyl, *S*(XI), and appreciably greater than that of N,N-di-*n*-butyl, *S*(XV).

Replacement of a hydrogen in the 2′-position of the Schiff base azo compound by a methyl or a methoxy group in the series (XI), (XII), (XIII);

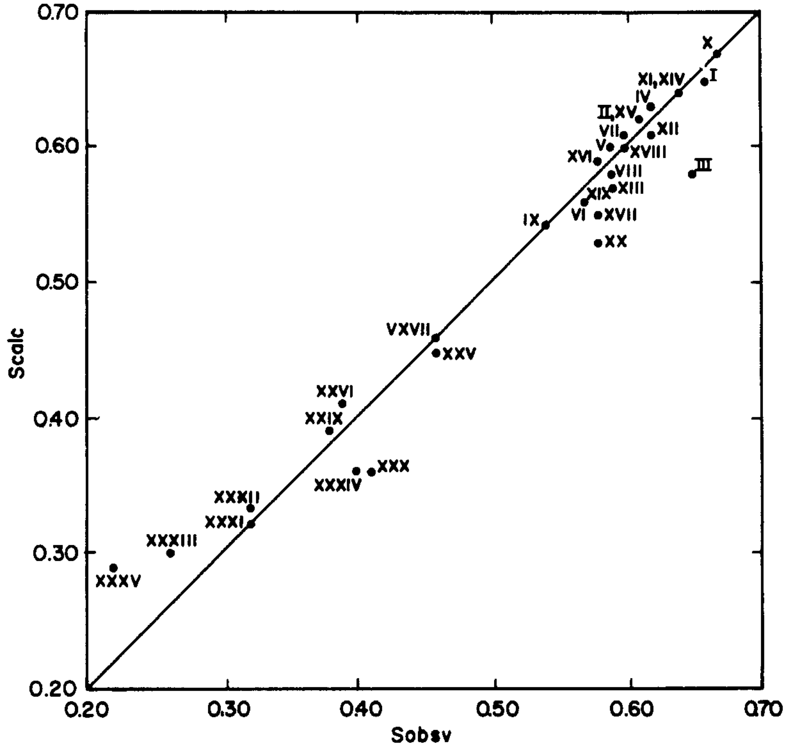


FIGURE 1 Calculated and observed order parameters for Schiff base azo compounds in Host *E*.

(XV), (XVI), (XVII); (XVIII), (XIX), (XX); (I), (II), (III); (IV), (V), (VI); and (VII), (VIII), (IX); results in markedly lower order parameter values. There are two effects which combine to lower the order parameters in 2′-substituted Schiff base azo compounds. Firstly, the introduction of an auxochrome in the lateral position of a Schiff-base azo compound may lead to a change in the absorption polarization direction. The absorption axis will no longer correspond with the alignment direction of the host. Secondly, the substitution of a group bulkier than hydrogen in a lateral position prevents the long axis absorption direction from aligning as well with the host direction. The effect of end group and phenyl ring substitution on lateral interactions, and thereby on S, are cumulative.[7] Using 4-nitro-4′-N,N-dimethylaminoazobenzene as the parent compound with an $S = 0.53$ in Host *E*, the effect of selected structural features on incremental changes in the order parameter (ΔS) were empirically derived and compiled in Table VI. S(calcd) was obtained by using the formula

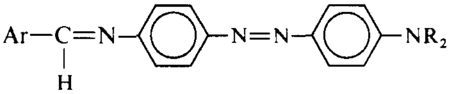
$$S(\text{calcd}) = 0.53 + \Sigma\Delta S \qquad (2)$$

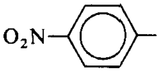
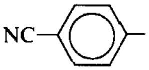
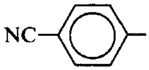
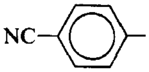
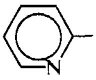
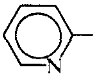
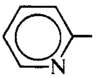
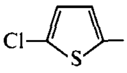
A plot of calculated *vs* observed order parameters in Host *E* for Schiff base azo compounds I–XX and some of their amine precursors is given in Figure 1. A line of slope = 1 which passes through the origin demonstrates that agreement between observed and calculated value is good.

Several points of interest are noted from the trend in the ΔS values of these dyes in the two different hosts. Firstly, the largest increase in S is observed on increasing the length of the molecular axis. Both the arylazo moiety ($\Delta S = 0.16$) and the arylazomethine moiety ($\Delta S = 0.15$) give very similar changes in Host *E*. Dyes dissolved in Host *E* are more sensitive to

TABLE V

Order parameters and absorption maxima of Schiff base azo dyes in Host *S*.

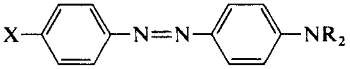


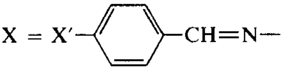
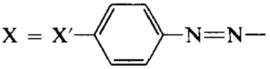
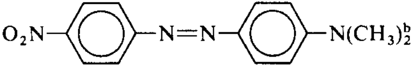
Dye	Ar	*R*	*S*	λ(nm)[a]
IV		n-C_4H_9	0.67	480
X		CH_3	0.70	460
XIV		$(CH_2)_2$ N-pyrrolidinyl	0.73	475
XV		n-C_4H_9	0.65	468
XXI		CH_3	0.67	440
XXII		C_2H_5	0.60	460
XXIII		n-C_4H_9	0.55	465
XXIV		n-C_4H_9	0.63	472

[a] Absorption Maximum in the nematic host.

TABLE VI

Parameters for calculating S



Structural feature	ΔS[a] (Host S)	ΔS (Host E)
$X = NO_2$	0	0
$X = CN$	-0.02	-0.01
	[c]	$+0.15$
	$+0.10$	$+0.16$
$X = NH_2$	[c]	-0.11
$Y = H$	0	0
$Y = CH_3$	-0.09	-0.03
$Y = OCH_3$	-0.15	-0.07
$R = CH_3$	0	0
$R = (CH_2)_2$	0	-0.03
$R = C_{(2+n)}H_{(5+2n)}$ ($n = 0, 1, 2 \ldots$)	$(-0.07\text{-}0.02n)$	$(-0.03\text{-}0.01n)$
	$S = 0.62$	$S = 0.53$

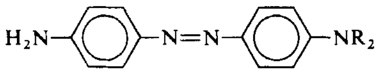
[a] Values taken from Ref. 7.
[b] Parent compound.
[c] Exchange reactions occurring, see text.

changes in the length of the dye molecular axis than they are in Host S. For the arylazo moiety $\Delta S = 0.16$ is obtained in Host E, while ΔS is only 0.10 for the same moiety in Host S. Secondly, substitution by a group bulkier than hydrogen in a lateral position generally lowers the order parameter.[7] However, this effect is more pronounced in Host S than in Host E. For instance, a decrease in the order parameter for the methoxy group is 0.15 in Host S, while a decrease of 0.07 is observed in Host E. Thirdly, the order parameter decreases about twice as much on increasing the length of the N-alkyl groups in Host S as in Host E. Fourthly, the parent compound has a significantly larger order parameter in Host S ($S = 0.62$) than in Host E ($S = 0.53$). These results re-emphasize[7, 8] the care which must be examined in interpreting order parameter data. The differing impact upon S of substitutions on different molecular positions of the guest may be useful for probing the solvating process in different hosts.

The order parameter of some 4-amino-4′-dialkylaminoazobenzenes in Host S shown in Table VII are exceptionally large with order parameters ($S \sim 0.7$) comparable in magnitude to those of Schiff base azo dyes in

TABLE VII

Order parameters and absorption maxima of 4-amino-4′-dialkylaminoazobenzenes in host *S*



Dye	*R*	*S*	λ(nm)[a]
XXXVI	CH_3	0.67	443
XXXVII	n-C_4H_9	0.65	460
XXXVIII	$(CH_2)_2$ pyrrolidinyl	0.70	465

[a] Absorption maximum in the nematic host.

Host *S* summarized in Table V. Also, the variations in order parameter for a number of similarly substituted 2-pyridyl Schiff base azo dyes (XXI), (XXII), and (XXIII) in Table V are much larger than expected from the empirically derived ΔS values. These anomalies cannot be rationalized in terms of the effect of dye structure, but can be explained in terms of exchange reactions between the amine or the amine moiety of the Schiff base guest molecules with the amine moiety of the Schiff base host molecules.[17] Further evidence for the Schiff base interchange comes from the fact that the order parameters in Host *E* increase by an average of about 0.2 on going from the amine compounds to the corresponding Schiff base azo compounds whereas similar changes do not cause any appreciable change in order parameter in Host *S*. Examination of the absorption maxima (λ_{max}) of the amino compounds in Tables III and VII shows considerable difference ($P\Delta_{max} \sim 20$ nm) in changing from Host *E* to Host *S*. The absorption maxima for all the amines examined in Host *E* lie between 420–428 nm. These amines undergo a bathochromic shift in Host *S* with absorption maxima in the 443–465 nm range. However, the corresponding nitro compounds show no appreciable difference in λ_{max} and very little change ($\Delta S < 0.07$) in order parameter in the two different hosts. The shift in λ_{max} on going from the amino compound to the corresponding Schiff base is about twice as much in Host *E* than in Host *S*. These results suggest that the amine dye guest molecules or the amine moiety of the Schiff base azo dye guest are exchanging with those of the Schiff base host molecules leading to an equilibrated mixture.

The effect of the aromatic group in a given class of Schiff base azo compound on order parameters in Host *S* is demonstrated by (XV), (IV), (XXIV), and (XXIII) in Table V. The order parameters decrease in the order 4-nitrophenyl > 4-cyanophenyl > 5-chlorothienyl > 2-pyridyl. This is the same order as the bathochromic effects of these groups on the absorption spectra of Schiff base azo dyes.[16] The order parameters and absorption maxima of these compounds in Host *S* are suspect because of exchange reactions which can occur among Schiff bases.[17]

CONCLUSIONS

We have investigated the correlations between the order parameter and the molecular structure for a number of Schiff base azo compounds in two different nematic liquid crystalline hosts by varying the structural characteristics of the dye molecules. We find an additivity of substituent effects which leads to good agreement empirically derived and observed *S* values in Host *E*. We have also shown that order parameters are host dependent. Comparison of the order parameters in Host *S* and Host *E* shows that Host *E* is more sensitive to the length of the molecular axis and less sensitive to lateral substituents while the reverse is true for Host *S*. The anomalously high order parameters of amines in Host *S* is ascribed to exchange reactions between the amine with the Schiff base mixtures in the host leading to formation of additional Schiff bases. The additivity of substituent effects no longer holds in cases where Schiff base exchange reactions can occur between the guest and host molecules. The results of this work corroborate our earlier reported findings concerning the effect of dye structure on order parameter in a nematic liquid crystalline host[7] and the effect of host on pleochroic dye order parameter.[8]

Acknowledgement

We wish to thank Dr. D. L. Ross, Dr. R. Williams, Dr. D. Meyerhofer, and Professor J. SanFilippo, Jr., for comments.

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10. The S value determined using this equation can only be regarded as a qualitative measure of the dye order parameter. It does not give the absolute order parameter of the guest-host interaction; A. Bloom and E. B. Priestly, *IEEE J. Electron Device*, **24**, 823 (1977). A number of workers have suggested that it is appropriate to correct the dye order parameter for the refractive index anisotropies of the host; see L. M. Blinov, V. H. Kizel, V. G. Rymyantsev, and V. V. Titov, *J. Phys. (Paris)*, **36**, (Cl, Suppl. 3), 69 (1975); H. Wedel and W. Haase, *Ber. Bun. Ges.*, **80**, 1342 (1972). A very small difference ($<1\%$) was noted between the order parameter observed using formula (1) and that corrected for the refractive index anisotropies of the host for a number of azo dyes in different nematic liquid crystalline hosts.[8]
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